(12) UK Patent (19) GB (11) 2 231 595 (13) B

(54) Title of Invention

Biological de-inking method

(51) INT CL[5]; **D21C 5/02**

(21) Application No
8929346.8

(22) Date of filing
29.12.1989

(30) Priority Data

(31) **6514**

(32) **16.05.1989**

(33) **KR**

(43) Application published
21.11.1990

(45) Patent published
24.03.1993

(52) Domestic classification
(Edition L)
D2W WH W324 W326

(56) Documents cited
EP0262040 A1

(58) Field of search

As for published application
2231595 A *viz:*
UK CL(Edition J) **D2W WC WH**
INT CL[4] **D21C**
updated as appropriate

(72) Inventor(s)
Tae Jin Eom
Steven Say-kyoun Ow

(73) Proprietor(s)
Korea Research Institute of Chemical Technology

(Incorporated in the Republic of Korea)

No. 100 Jang-dong
Usung-ku
Daejonjikhal-shi
Republic of Korea

(74) Agent and/or
Address for Service
Saunders & Dolleymore
9 Rickmansworth Road
Watford
Herts
WD1 7HE
United Kingdom

BIOLOGICAL DE-INKING METHOD

This invention relates to a process for reclaiming useful pulp fibers from wood containing or wood free wastepaper by a biological method in the de-inking process.

De-inking of pulp fibers is essentially a laudering or cleaning process in which the ink is considered to be the dirt.

Chemicals along with heat and mechanical energy, are used to dislodge the ink particles from fibers and to disperse them in an aqueous medium. The ink particles are then separated from the pulp fibers, either by washing or floatation or by using a modern hybrid process that combines the two elements.

The chemicals used for the conventional de-inking process are surfactants which functions are detergency to remove ink from fiber, dispersing action to keep the ink particles dispersed and prevent redeposition on the fibers, and foaming action in the froth floatation of ink particles.

A typical surfactant is a long chain molecule with the hydrophobic part to the one end and the hyrophilic part to the other end. The hydrophobic part may consist of a fatty acid, fatty alcohol, alkylphenol or other oil-soluble surfactant.

The hydrophilic part in the de-inking surfactant usually consists of anion molecules such as carboxyl acid salts or sulfonic acid salts and nonionic molecules such as polyoxyethylenated chains.

The typical surfactants commonly used in the washing and froth floatation de-inking processes are ; sodium and potassum salts of straight-chain

fatty acids (soap), linear alkylbenzenesulfonates (LAS), - olefine sulfonates, long-chain fatty alcohols, polyoxyethylenenated alkylphenols, alkylphenolethoxylates, and polyoxyethylenated straight-chain alcohols.

Major disadvantages of using these surfactants in the de-inking process are excess foaming in the subsequent pulp stock flow and papermaking process lines. Some of the above surfactants are resistant to biodegradation in the effluent treatment stages causing a serious environmental problem.

In the froth floatation de-inking process, a collector is added to agglomerate ink into large particles and attach them to the air bubbles. Collectors are required for effective floatation and are usually anionic long-chain fatty acid soaps. Fatty acid collectors are precipitated with calcium ions to form larger, insoluble ink particles and collector particles. With injection of air in the floatation cells, the agglomerated ink particles adhere to the bubbles, rise to the surface and are skimmed off from the system.

Major disadvantages of the floatation method using the fatty acid collector is a pitch deposition and calcium scaling problems in the subsequent stock lines and papermaking process equipment. Besides the surfactants, other chemicals are caustic soda, sodium silicate, metal ion chelating agents and hyrodgen peroxide.

The hydrogren peroxide bleaching agent has to be added in order to prevent a pulp color yellowing caused by the addition of caustic soda and to improve brightness of pulp fibers.

With advances in modern printing and

photocopying technology conventional de-inking with the aid of surfactants encounters serious problems with wastepaper printed with the use of heavily coated, highly polymerized, or nonimpact inks, such as ultraviolet, heatset, Xerox, (Registered Trade Mark) laser and ink jet. These inks usually contain cured polymer resins which bind ink particles so strongly on the fiber surface that it is impossible to dislodge the inks completely during the wastepaper defiberizing (pulping) stage with the conventional de-inking chemicals. Excess heat and mechanical energy are also required along with the ineffective conventional chemicals.

In the conventional floatation de-inking process for newsprint wastepaper a major technial problem arises from fine ink particles embedded in the fiber bundles and between fibrils which are almost impossible to remove from the fibers by a washing and/or floatation process.

This invention provides a new and much improved de-inking method which is effective in newsprint de-inking as well as the wood free printed wastepaper such as whiteledger, laser printed, xerographic copypaper and computer printout wastepaper.

This invented de-inking method is to remove ink paticles using the biological activity of enzymes on the cellulose fiber surface and the dispersing function of enzyme proteins on ink particles.

In contrast to the conventional method no alkali and de-inking surfactants are required although some surfactants can be used along with the enzyme to enhance the de-inking efficiency. In the froth floatation process the fatty acid collectors are not required. Since caustic soda is not used in the newsprint de-inking, hydrogen peroxide bleaching

agent is also not required for yellowing prevention.

The elimination of the fatty acid collector in this biological de-inking process will solve the persistent pitch and scale deposition problem associated with the conventional floatation process using the fatty acid type soap and calcium salts and silicates.

The process of the invention is described in detail as follows:

The newspaper such as old newsprint or printed wood free wastepaper is disintergrated in a conventional pulper (consistancy 4-7%) or in a high consistency pulper, 12-15%, at a water temperature ranged from room temperature up to 60°C. The added level of enzyme is 0.005% to 5.0% based on the dry weight of wasepaper, pH of the stock slurry is adjused in the range of 3.0 to 8.0. As compared to the conventional pulping process using caustic soda and surfactants the pulping in the enzyme process can be completed in a relatively short period and ink particles are completely seperated from the fiber surface and dispersed well. The dispersed inks are removed from the pulp fibers by conventional washing process equipment such as vibration screen and drum washers without the aid of detergent surfactants in single and multi stages. The ink patricles dispersed with the action of an enzyme protein can be also selectively removed from the diluted pulp slurry with conventional floatation equipment in which air is injected or drawn into the pulp to provide bubbles to pick up the particles. No fatty acid collector is required in the case of waste newsprint. But a small amount of fatty acid collector may be added to enhance the ink removal efficiency in the case of laser-printed wastepaper.

This biological de-inking process lowers pulping energy to a large extent since the addition of an enzyme results in a substantial reduction in pulping time as compared to pulping in the absence of enzymes, almost 50% reduction. The observed faster and easier pulping in the presence of enzymes may be attributed to the unique biological activity of enzymes which is effective to debond the fiber bonding and dislodge the inks bonded on the fiber surface as well as within the fiber bundles or between the fibrils. A partial enzymatic hydrolysis of cellulose within the micro structure of fiber surface may occur during the pulping stage. Because of the biological activity of enzymes the fine ink particles embedded within fiber bundles, fibrils and fines which had been impossible to take out by conventional de-inking chemicals in the case of old newsprint de-inking, is now possible.

According to this biological de-inking method of old newsprint, the addition of hydrogen peroxide to prevent fiber yellowing is not required, which will result in a substantial reduction of de-inking chemcial cost as compared with the conventional de-inking process using caustic soda, hydrogen peroxide, chelating agent and sodium silicates.

It should be pointed out that the physical strength properties of the resulting pulp fiber prepared by this invented method are found to be higher than those of the corresponding pulp prepared by the conventional method in addition to the much higher resulting pulp brightness. The enzyme addition does not appear to degrade the fiber strength, instead improve the fiber strength by as yet an unknown mechanism.

Example 1

De-inking of old newsprint with a cellulolytic enzyme

A sample of old newsprint wastepaper was added to the pulper which was filled with 40°C water at a consistancy of 4% and a cellulase enzyme was dissolved at a dosage level of 0.1% based on oven dry weight of wastepaper. The wastepaper was soaked for 10 minutes and then disintergrated for 5 minutes. After a complete disintergration of wastepaper, one half of pulp slurry was diluted to 1% consistency.

The diluted pulp slurry was moved to the air floatation cell and then the dispersed ink particles were removed from the pulp slurry by skimming off the ink particle froth from the cell while injecting air through a porous plate. The floatation time for the complete removal of the ink froth was one minute.

The other half of the pulp slurry was washed on a laboratory vibration screen to remove the dispersed ink particles.

The resulting recycled pulp fibers obtained by the floatation and washing step were evaluated for pulp brightness and mechanical strength properties. To compare this enzyme-treated de-inked pulp to the conventional de-inked pulp, the same sample of watepaper was treated in the pulper with addition of 1.0% NaOH, 0.3% H_2O_2, 3% sodium silcated solution (water glass) and 0.8% of SERFAX (Registered Trade Mark) MT-90 (fatty acid soap) and 0.2% IGEPAL-660 based on oven dry weight of wastepaper. The pulping time was 10 minutes for a complete disintergration. After diluting to 1% consistancy, the dispersed ink particles were removed by the floatation method with the laboratory floatation cell in the way described above.

As shown in Table 1, the brightness of the pulp de-inked with an enzyme was much higher than that of the pulp de-inked with conventional chemicals and the mechanical strength of the enzyme-de-inked pulp was also superior to that pulp de-inked with the fatty acid collector and the dispersant (IGEPAL-660). Microscopic observation revealed that the pulp prepared by the present invention contained more long fiber fractions, had a smoother fiber surface and looked less mechanically damaged.

Table 1. Comparison of properties of recycled pulp by method of the present invention and the conventional method.

		brightness (%)		tensile index (N.m/g)		tear index (mN.m/g)	
		KONP	AONP	KONP	AONP	KONP	AONP
present method	flotation	47.1	45.2	28.9	32.4	11.7	13.6
	washing	50.3	48.6	29.3	32.9	11.8	14.1
SERFAX MT90		45.1	38.4	30.1	32.8	10.8	13.1

KONP; Korean old newspapwe.
AONP; American old newspaper.
SERFAX is a Registered Trade Mark.

The enzyme treated pulp gave cleaner and brighter pulp with washing as compared to the floatation ink removal.

The enzyme addition appeared to accelerate the wastepaper disintergration to a large extent. When the old newspaper was disintergrated in the conventional pulper at the 4% consistency, the addition of 0.5% enzyme reduced the pulping time from 5 minutes (no enzyme added) to 30 seconds for a complete disintergration as shown in Table 2.

Table 2. Relation between enzyme addition and disintergration time.

enzyme (%)	0.5	0.1	0
disintergration time (sec)	30>	60-120	300<

Example 2

De-inking of laser CPO (computer printout) with a cellulolytic enzyme.

It is almost impossible to achieve a complete removal of laser beam cured ink particles from laser CPO wastepaper with conventional de-inking chemicals, because the ink particles are so strongly adhered to the fiber surface that alkali and general de-inking surfactants of the conventional type are not able to dislodge and disperse the ink particles in the pulp-water slurry.

A sample of laser-CPO wastepaper was added to water in a laboratory high consistency pulper at a consistency of 12.5% and a cellulase enzyme was

added to the water at a dosage level of 0.2% based on the dry weight of paper. At stock water temperature of 20-35°C, the pulping was carried out for 20 minutes. The completely disintergrated pulp slurry was diluted to 0.5% and then the dispersed ink particles removed from the pulp slurry using the laboratory floatation cell in the same way as in Example 1. In this case, to increase the ink removal efficiency and selectivity a small amount of a conventional fatty acid collector, SERFAX (Registered Trade Mark) MT-90, 0.3% based on dry weight of wastepaper was added prior to the air floatation and the floatation time was 3 minutes. To compare with enzyme de-inked pulp, conventional de-inked pulp was prepared by the same way but under different chemical conditions as follows:

1% NaOH on dry weight of wastepaper
0.1% IGEPAL 660 dispersant
0.8% SERFAX (Registered Trade Mark) MT-90
pulping temperature ; 50°C
pulping time ; 30 minutes
calcium salt addition to the flotatin cell; 200 ppm
floatation time ; 3 minutes

The brightness and the strength properties of the resulting pulp samples are compared in Table 3.

As shown in the table, the image analysis of the paper samples indicates that the number of residual ink particles was much less, about 10 times, for the pulp de-inked with the enzyme and the tensile strength was also higher as compared to the pulp prepared with conventional chemicals.

The recycled chemical pulp of high quality in terms of dirt count and fiber strength properties can be obtained with the use of an enzyme in

combination of a small amount of fatty acid collector by the floatation method.

Table 3. Comparison of pulp properties recycled by the method of the present invention and the conventional method.

	brightness (%)	dirt amount (count/area)	tensile index (N.m/g)
enzyme+MT-90(0.3%)	79.0	450	34.3
MT-90 (90%)	80.6	4,330	26.3

Example 3.
De-inking of waste newsprint by a pectinolytic enzyme.

Using the same method as example 1, the waste newsprint containing 0.1% of the enzyme pectinase was soaked for 10 minutes at 40°C and disintergrated for 5 minute. Diluting the disintergrated pulp to 1%, ink particles are removed by floatation for 1 minute.

As shown in Table 4, the brightness and the tensile strength of paper sheet prepared by the method of present invention are improved.

Table 4. Comparison of the method using a pectinolytic enzyme with the conventional method.

	brightness (%)	tensile index (N.m/g)
present method	44.2	33.3
MT-90 (0.8%)	38.4	32.8

What we claim is ;

1. Biological de-inking method characterised by pulping printed paper together with an enzyme and removing the ink particles by floatation and/or washing.

2. A method according to Claim 1 in which a cellulase enzyme is used.

3. A method according to Claim 1 in which the enzyme pectinase is used.

4. A method according to any one of Claims 1 to 3 in which the amount of enzyme is in the range of 0.005% to 5% based on the dry weight of printed paper.

5. A method according to any one of the preceding claims in which the paper is pulped at a temperature in the range of room temperature to 60°C.

6. A method according to any one of the preceding claims in which the paper is pulped at a pH in the range 3 to 8.

7. A biological de-inking method using an enzyme substantially as hereinbefore described with reference to any one of examples 1 to 3.